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(54) METHOD FOR PRODUCING GAS GENERATING AGENT

VERFAHREN ZUR HERSTELLUNG EINES GASERZEUGENDEN MITTELS

PROCEDE DE PRODUCTION D'UN AGENT GENERANT DU GAZ

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(56) References cited:
EP-A1- 0 458 443 EP-A1- 0 694 511
EP-A1- 0 949 225 EP-A1- 1 061 057
EP-A2- 0 458 439 EP-A2- 0 820 971
WO-A1-00/44690 WO-A1-01/04074
WO-A1-96/22954 WO-A2-98/06486
JP-A- 9 110 574 JP-A- 10 087 390
JP-A- 11 310 490 JP-A- 2000 095 592
JP-A- 2000 103 692 US-A- 5 608 183
US-A- 5 735 118

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Description

[0001] The present invention relates to a process for producing a gas generating agent particularly suitable for use in inflators for airbags installed in vehicles.

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Prior Art

[0002] Known inflators in an inflatable type safety system (airbag system) for automobiles include a pyrotechnic inflator expanding an airbag only with a gas generated by combustion of a gas generating agent, a hybrid inflator expanding an airbag by pushing out a pressurized gas charged previously with a heat and pressure generated by combustion of a gas generating agent, and further, an inflator using the both in combination.

[0003] The gas generating agent used in these inflators is demanded to have various properties such that toxic components in a gas generated by combustion is restricted to be minimum, that good thermal stability is maintained with a passage of time, and that generation of mists is restricted to be minimum, etc., which are influenced by the composition of the starting components. Accordingly, in production of the gas generating agent, it is important to consistently provide the article having these properties, and it will be more desirable if the production process can also contribute to these properties.

[0004] US-A 5,487,851 and US-A 5,565,150 are known as relevant prior arts, but use of organic solvents is essential for inventions described in these patent specifications. Therefore, there is a problem in safety because the possibility of occurrence of fires cannot be eliminated, and there is also a problem with recovery of organic solvents and deterioration in the working atmosphere. In addition, US-A 5,670,098 discloses a method of producing black powder.

[0005] JP-A-10-87390 relates to a gas generating agent having a small linear burning rate. The gas generating agent comprises a nitrogen-containing organic compound, an oxidizer, a slack forming agent and a binder. Further disclosed is a process for producing the gas generating agent, wherein the process comprises the extrusion molding of a wet slurry of the starting compounds by adding water to the starting compounds, followed by extrusion molding and a drying step.

[0006] JP-A-9-110574 relates to a gas generating agent for an airbag and a production thereof. A mixture including a combustion catalyst of a metallic oxide or a sulfide together with an oxidizer and a binder is mixed, followed by extrusion and a drying step. The binder may be an aqueous solution, which is added to the mixture prior to extrusion, followed by a drying step.

[0007] JP-A-11-310490 relates to a gas generating composition and a production method thereof. A mixture is extrusion molded, and the mixture contains a nitrogen-containing organic compound as an oxidizer together with a fuel component.

[0008] EP-A-458443 discloses a process for manufacturing a gas generating material comprising the steps of a) preparing a wet mixture of a metal acid and a metal oxide without prior mixing of the metal acid and the metal oxide in dry form, processing the wet mixture to form granules of gas generating material; b) drying the granules of gas generating material; and c) maintaining the mixture in a wet state throughout said processing prior to said step of drying the granules.

[0009] EP-A-458439 relates to a process for making a body of gas generating material, wherein the extrusion step is carried out using an extruder having twin transport screws.

[0010] WO-A-9622954 relates to methods for processing gas generant compositions to produce fuse box. The mixing step may be carried out using a twin-screw extruder.

[0011] US-A-5735118 discloses a method of inflating an inflatable air bag or balloon comprising the steps of generating substantially non-toxic gas by combusting an at least essentially azide-free gas generating composition containing at least one metal amine complex having transition metal cation or alkaline earth metal cation and at least one neutral ligand comprised of ammonia, and sufficient oxidizing anion to balance the charge of the metal cation, wherein said composition is formulated with at least one additional ingredient which comprises (i) carbon powder, (ii) a binder, or (iii) up to about 50% by weight of an inorganic oxidizer, such that when the gas generating formulation combusts, a substantially non-toxic mixture of gases containing nitrogen gas and water vapor is produced; and inflating said air bag or balloon using said gases.

[0012] EP-A-820971 discloses a gas-generant-molded-article for air bags having a cylindrical form containing an opening hole, wherein the relationship between the linear burning velocity r (mm/second) of said gas generant composition under a pressure of 70 kgf/cm² and a thickness W (mm) of said molded article falls within a range represented by $0.005 \leq W/(2 \cdot r) \leq 0.3$.

[0013] EP-A-1061057 relates to a gas generating composition comprising a fuel component, an oxidizing agent and at least one additive, which further comprises nitrogenous organic compound used as said fuel component, ammonium perchlorate and nitrate of alkaline metal or alkaline earth metal used as said oxidizing agent and in which where a quantity of nitrate required solely for forming an oxide of alkaline metal or alkaline earth metal that can stoichiometrically neutralize hydrogen chloride generated from ammonium perchlorate is taken as 1, a quantity of nitrate of said alkaline metal or alkaline earth metal exceeds 0.9.

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[0014] WO-A-9806486 relates to a gas generating composition wherein metal complexes are used, said complexes being comprised of a metal cation template, a neutral ligand containing hydrogen and nitrogen, sufficient oxidizing anion to balance the charge of the complex, and at least one cool burning organic nitrogen-containing compound.

[0015] US-A-5608183 relates to a gas generant composition comprising a fuel, and an oxidizer comprising a specific nitrate salt of a polyamine.

[0016] EP-A-0694511 discloses a gas generating composition essentially containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizing agent and further containing an oxide-based catalyst comprising at least two members selected from the elements of Groups I, IV, V, VI, VII and VIII in the periodic table.

Disclosure of Invention

[0017] An object of the invention is to provide a process for producing a gas generating agent which can reliably and stably exhibit properties required of its starting composition.

[0018] The present invention provides a process for producing a gas generating agent, comprising a first step of feeding at least two starting components including a fuel and an oxidizing agent and stirring and mixing them in the presence of moisture, wherein the fuel is a nitrogen-containing compound, wherein the oxidizing agent is a basic metal nitrate, wherein the moisture is ion-exchanged water and/or distilled water, and wherein an amount of moisture in the mixture of the starting components is adjusted to 5 to 60% by weight; a second step of extrusion-molding the mixture and cutting it, a third step of drying it, wherein the mixture is dried so that an amount of moisture in the gas generating agent is reduced to 0.7% by weight or less, and wherein the process further includes an aging step of keeping the mixture at 30 to 50°C for 8 hours or more between the first and second step.

[0019] In the present invention, the "moisture" means the sum of a moisture initially present in the two or more starting components and a moisture fed to the starting components.

[0020] The "mass reduction by heating" means the reduced mass of a molded article of the gas generating agent after being kept at 120°C for 120 minutes when a moisture is used as the solvent, and this reduced mass ratio essentially means a reduction in the moisture, which is determined by a halogen moisture meter. When an organic solvent other than moisture is used as the solvent, the boiling point of the organic solvent should be taken into consideration, and simultaneously the temperature and time achieving the desired mass reduction by heating are determined such that the finally obtained gas generating agent can satisfy qualities required of the article.

[0021] According to the process of the present invention, there can be constantly provided a high-quality gas generating agent.

Preferred Embodiment of the Invention

[0022] The process for producing the gas generating agent of the present invention comprises the first, second and third steps described above, and a procedure ordinarily carried out in producing a gas generating agent by those skilled in the art can be additionally carried out before and after each of the steps described above. Unless otherwise specified, each step described below can be applied to both batch and continuous systems.

[0023] The first step is the step of feeding two or more starting components containing fuel and an oxidizing agent and stirring and mixing them in the presence of moisture. In the treatment in the first step, any of the following methods can be suitably selected as the method of feeding two or more starting components and moisture.

- (i) A method in which each of the two or more starting components are fed with a necessary amount of moisture and then mixed.
- (ii) A method in which two or more starting components and a necessary amount of moisture are simultaneously fed and then mixed.
- (iii) A method in which two or more starting components are mixed and simultaneously fed with a necessary amount of moisture.
- (iv) A method in which two or more starting components are preliminarily mixed, then fed with a necessary amount of moisture, and further mixed.
- (v) A method in which, in the methods (i) to (iv), a necessary amount of water is fed by spraying.

[0024] In the first step, ion-exchanged water and/or distilled water is used as the moisture to be fed.

[0025] The ion-exchanged water and/or distilled water are those having an electrical conductance of not higher than 2 μ S/cm wherein metal ions, for example alkali metal ions such as Na, K, Li, etc., alkaline earth metal ions such as Mg, Ca, etc., and other metal ions are reduced. Water, etc. not containing metal ions as described above are used for the following reason; for example, when moisture contains Na ions as metal ions, the Na ion can form NaOH which can remain in the gas generating agent to cause decomposition of the starting components such as fuel, etc. by hydrolysis

reaction, which may result in a deterioration in the thermal stability of the gas generating agent itself.

[0026] An amount of moisture added in the first step is determined in consideration of an amount of the moisture contained initially in the starting components used, and an amount of moisture in the mixture of the starting components at the time of mixing is adjusted to 5 to 60% by weight. When the batch system is employed, preferably, an amount of moisture is 30 to 60% by weight, more preferably 30 to 40% by weight. When the continuous system is employed, preferably, an amount of moisture is 10 to 30% by weight, more preferably 10 to 20% by weight.

[0027] When an amount of moisture at the time of mixing is lower than the upper limit, the adjustment of moisture can be facilitated and simultaneously productivity can also be improved. When an amount of moisture is higher than the lower limit, the mixing operation can be carried out smoothly and a preferable binder effect can be given, thus facilitating the molding procedure and preventing cracking of the molded article or significant roughness of the surface of the molded article.

[0028] Conditions of mixing two or more starting components with moisture in the first step are that a mixing temperature is preferably 20 to 100°C, more preferably 40 to 80°C, and a mixing time is preferably 10 to 120 minutes, more preferably 30 to 60 minutes in the batch system, or preferably 1 to 10 minutes in the continuous system.

[0029] When the process of the invention is carried out in the batch system, part of the moisture can be removed by volatilization while the components are mixed, and after the components are mixed, part of the moisture can also be removed by volatilization.

[0030] At the time of removing part of moisture by volatilization, the moisture can be removed by volatilization at a higher temperature by preferably 0 to 80°C, more preferably 10 to 30°C. Further, in case of removing part of moisture by means of volatilization to facilitate treatments in later steps, an amount of the moisture in the mixture of the starting components is adjusted to preferably 5 to 30% by weight, more preferably 10 to 30% by weight, still more preferably 10 to 20% by weight.

[0031] When two or more materials and moisture are mixed in a mixer in the first step, a method of degassing through a vent hole of the mixer, if required, under suction can be used as a method of removing part of the moisture.

[0032] When the process of the invention is carried out in the batch system, cooling treatment can be additionally carried out to facilitate handling in the post-step (aging treatment) after part of the moisture is removed by volatilization under mixing as described above. In this cooling treatment, a temperature of the mixture is reduced to preferably 30 to 65°C, more preferably 30 to 50°C after cooling.

[0033] The cooling method is not particularly limited, but when two or more starting components and moisture are mixed in a mixer in the first step, such a method can be employed that reverse rotation and forward rotation of stirring are suitably combined. When one stirrer is used, the "reverse rotation" or "forward rotation" means that the stirring direction (rotating direction) is made different. And when two stirrers are used, the "reverse rotation" means that one (e.g. the left stirrer) of the two adjacent stirrers is rotated in the clockwise direction and the other (the right stirrer) is rotated in the anticlockwise direction, while the "forward rotation" means that the left stirrer is rotated in the anticlockwise direction and the right stirrer is rotated in the clockwise direction.

[0034] When the process of the invention is carried out in the batch system, a step of aging the mixture can be additionally carried out between the first and second steps, in order not to make uneven parts in temperature and moisture of the mixture and further, in order to regulate the temperature so as to facilitate extrusion molding.

[0035] The aging treatment is carried out by keeping the mixture at 30 to 50°C, preferably at 35 to 45°C and for 8 hours or more, preferably 16 hours or more.

[0036] The aging treatment can be carried out in the mixing machine used in the first step or it can be carried out after transferring the mixture to another container which is capable of maintaining the mixture under predetermined conditions.

[0037] The second step is a step of extrusion-molding and cutting the mixture obtained in the first step from two or more starting components and moisture. When the batch system is employed, the mixture after the first step or the subsequent aging step is extrusion-molded by an extruder.

[0038] Extrusion-molding is not particularly limited, and a method of molding at one stage or a method of molding at two or more divided stages including pre-molding can be used. In case of one-stage molding, a molding pressure is preferably 70 MPa or less, more preferably 60 MPa or less. And in case of two-stage molding, a pre-molding pressure is preferably 70 MPa or less, more preferably 60 MPa or less, and further, a molding pressure is preferably 70 MPa or less, more preferably 60 MPa or less.

[0039] In the first step, an amount of moisture in the mixture of the starting components before extrusion-molding is preferably adjusted to 5 to 30% by weight, more preferably 10 to 30% by weight, still more preferably 10 to 20% by weight. When an amount of moisture in the mixture of the starting components at extrusion-molding is less than 5% by weight, additional moisture is desirably added to adjust an amount of moisture to the above range.

[0040] When an amount of moisture at extrusion-molding is less than the upper limit, a molding procedure is made easy and a molded article is not deformed. When an amount of moisture is higher than the lower limit, a preferable binder effect can be given, thus facilitating a molding procedure and preventing cracking of a molded article or significant roughness of the surface of a molded article.

[0041] In a cutting procedure, the article is cut into pieces to meet required standards by a cutting machine or a cutting machine connected to the extrusion-molding machine.

[0042] The third step is a step of drying the molded article which is extrusion-molded and cut in the second step. In the batch and the continuous system, the drying treatment is carried out in a drying oven.

[0043] The drying treatment is carried out such that an amount of moisture in the gas generating agent is reduced to be preferably 0.5% by weight or less, more preferably 0.3% by weight or less.

[0044] The drying method is not particularly limited, and a method of drying at one stage or a method of drying at two or more divided stages including pre-drying can be employed. Preferably, one-stage drying is carried out at a temperature of 80 to 120°C, more preferably 90 to 110°C, And in case of two-stage drying, pre-drying is carried out preferably at 20 to 40°C, more preferably at 25 to 35°C, and then, drying is carried out preferably at 80 to 120°C, more preferably at 90 to 110°C.

[0045] The classification step of regulating the size of the gas generating agent can be additionally carried out after the third step by sifting the gas generating agent.

[0046] The treatment in the above-described steps in the process of the invention can be carried out, for example, by a combination of a mixer, a container for aging, an extruder, a cutting machine and a drying oven in case of the batch system, and by a combination of a twin-screw kneading and mixing extruder, a cutting machine (pelletizer) and a drying oven in the case of the continuous system.

[0047] When the continuous system is employed, it is preferable to use a twin-screw extruder in the first step (kneading and mixing step).

[0048] When the screwed twin-shaft extruder is used in the kneading and mixing step, a desired die can be attached to an extrusion orifice of the screwed twin-shaft extruder, and by changing a shape of the die hole, a molded article of desired shape in the form of a pellet, a single-perforated cylinder or a perforated (porous) cylinder can be obtained. For example, in order to obtain a molded article in the form of a single-perforated or perforated (porous) cylinder, a die consisting of a combination of a pin and a bushing is used.

[0049] After the article is thus molded in the kneading and mixing step, the molded article can be subjected to cutting at the outlet of the die in the subsequent step linked with extrusion-molding, or once formed into a plurality of molded articles in a stand form and then subjected to cutting.

[0050] When a screwed twin-shaft extruder is used, an amount of moisture in the mixture in the starting components inside the extruder is 5 to 60% by weight, preferably 10 to 30% by weight, more preferably 10 to 20% by weight. For the same reason as in the preferable range of an amount of the moisture at extrusion-molding, moisture in the extruder is regulated by degassing through a vent hole and the like so that an amount of moisture in the die attached to the extruder is reduced to be preferably 5 to 30% by weight, more preferably 10 to 30% by weight, still more preferably 10 to 20% by weight.

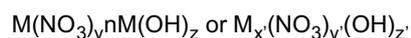
[0051] In the process of the invention, it is possible to use (a) fuel and (b) an oxidizing agent and (c) an additive if required as the two or more starting components. In this case, the content of the starting components in the following description is shown on a dry-weight basis.

[0052] As the fuel as component (a), a nitrogen-containing compound which is generally used as fuel in a gas generating agent is used. The nitrogen-containing compound can include one or at least two selected from the group consisting of tetrazole derivatives such as 5-aminotetrazole, bitetrazole derivatives such as bitetrazole diammonium salt, triazole derivatives such as 4-aminotriazole, guanidine derivatives such as dicyandiamide, nitroguanidine, guanidine nitrate, triazine derivatives such as trihydrazinotriazine, oxamide, ammonium oxalate, azodicarbonamide, hydrazodicarbonamide.

[0053] The guanidine derivatives can include at least one selected from the group consisting of guanidine, mono-, di- and tri-aminoguanidine nitrates, guanidine nitrate, guanidine carbonate, nitroguanidine (NQ), dicyandiamide (DCDA) and nitroaminoguanidine nitrate, and among these, nitroguanidine and dicyandiamide are preferable.

[0054] The oxidizing agent used as the component (b) is a basic metal nitrate.

[0055] The basic metal nitrates are a series of compounds represented by the formula below. Some compounds contain hydrates thereof, too.



wherein M represents a metal, x' represents the number of metals, y and y' each represent the number of NO₃ ions, z' represents the number of OH ions, and n represents a ratio of M(OH)₂ moiety to M(NO₃)_y moiety.

[0056] Examples of the compound corresponding to the above formula includes one or at least two selected from the group consisting of basic copper nitrates [(BCN)Cu₂(NO₃)(OH)₃, Cu₃(NO₃)(OH)₅·2H₂O], basic cobalt nitrate [Co₂(NO₃)(OH)₃], basic zinc nitrate [Zn₃(NO₃)(OH)₃], basic manganese nitrate [Mn(NO₃)(OH)₂], basic iron nitrate [Fe₄(NO₃)(OH)₁₁·2H₂O], basic molybdenum nitrate, basic bismuth nitrate [Bi(NO₃)(OH)₂] and basic cerium nitrate [Ce(NO₃)₃(OH)·3H₂O] containing copper, cobalt, zinc, manganese, iron, molybdenum, bismuth or cerium as a metal M,

and among these, a basic copper nitrate is preferable.

[0057] The basic copper nitrate has, in comparison with ammonium nitrate as an oxidizing agent, an excellent thermal stability because no phase transition occurs in the range of the use temperature and a melting point is high. Further, since the basic copper nitrate acts to decrease a combustion temperature of a gas generating agent, amounts of nitrogen oxides generated can be decreased.

[0058] When the gas generating agent comprises (a) fuel and (b) an oxidizing agent, a content of the component (a) is preferably 5 to 60% by weight, more preferably 15 to 55% by weight. A content of the component (b) is preferably 40 to 95% by weight, more preferably 45 to 85% by weight.

[0059] One preferable embodiment in case of including the components (a) and (b) includes one comprising (a) biterazole diammonium salt and (b) a basic copper nitrate. In this case, contents are preferably 5 to 60% by weight, preferably 15 to 55% by weight, more preferably 15 to 45% by weight or 15 to 35% by weight of (a) bitetrazole diammonium salt, and 40 to 95% by weight, preferably 45 to 85% by weight and more preferably 55 to 85% by weight or 65 to 85% by weight of (b) a basic copper nitrate.

[0060] Other preferable embodiment of the gas generating agent including the components (a) and (b) can be one comprising (a) nitroguanidine and (b) a basic copper nitrate. In this case, contents are preferably 30 to 70% by weight, preferably 40 to 60% by weight of (a) nitroguanidine, and 30 to 70% by weight, preferably 40 to 60% by weight of (b) a basic copper nitrate.

[0061] Still other preferable embodiment of the gas generating agent including the components (a) and (b) can be one comprising (a) dicyandiamide and (b) a basic copper nitrate. In this case, contents are preferably 15 to 30% by weight of (a) dicyandiamide and 70 to 85% by weight of (b) a basic copper nitrate.

[0062] As the additive as component (C), at least one selected from the group consisting of carboxymethyl cellulose (CMC), carboxymethyl cellulose sodium salt (CMCNa), carboxymethyl cellulose potassium salt, carboxymethyl cellulose ammonium salt, acetate cellulose, cellulose acetate butyrate (CAB), methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), ethyl hydroxyethyl cellulose (EHEC), hydroxypropyl cellulose (HPC), carboxymethyl ethyl cellulose (CMEC), fine crystalline cellulose, polyacrylamide, aminated polyacrylamide amide, polyacryl hydrazide, acrylamide-metal acrylate copolymers, copolymer of polyacrylamide and polyacrylate ester compound, polyvinyl alcohol, acrylic rubber, guar gum, starch, silicone, molybdenum disulfide, Japanese acid clay, talc, bentonite, diatomaceous earth, kaolin, calcium stearate, silica, alumina, sodium silicate, silicon nitride, silicon carbide, hydrotalcite, mica, nitrates (KNO_3 , NaNO_3 , etc.), perchlorates (KClO_4 , etc.), metal oxides, metal hydroxides, metal carboxylates, basic metal carbonates and molybdates can be proposed.

[0063] As the metal oxide, at least one selected from the group consisting of copper oxide, iron oxide, zinc oxide, cobalt oxide, manganese oxide, molybdenum oxide, nickel oxide and bismuth oxide can be proposed. As the metal hydroxide, at least one selected from the group consisting of cobalt hydroxide and aluminum hydroxide can be proposed. As the metal carboxylate or basic metal carboxylate, at least one selected from the group consisting of calcium carbonate, cobalt carbonate, basic zinc carboxylate, basic copper carbonate, basic cobalt carbonate, basic iron carbonate, basic bismuth carbonate and basic magnesium carbonate can be proposed. As the molybdate, at least one selected from the group consisting of cobalt molybdate and ammonium molybdate can be proposed. These compounds can act as slag-forming agents and/or binders. The binder in the form of aqueous solution in 1 % by weight preferably has a viscosity of 100 to 10,000 mPas.

[0064] To improve the ignitability of the gas generating agent, the carboxymethyl cellulose sodium salt and potassium salt are preferable, and the sodium salt is more preferable.

[0065] When the gas generating agent includes the components (a), (b) and (c), a content of the component (a) is preferably 5 to 60% by weight, more preferably 15 to 55% by weight. A content of the component (b) is preferably 40 to 95% by weight, more preferably 45 to 85% by weight. A content of the component (c) is preferably 0.1 to 25% by weight, more preferably 0.1 to 15% by weight, still more preferably 0.1 to 10% by weight.

[0066] A preferable embodiment of the gas generating agent including the components (a), (b) and (c) can be one comprising (a) nitroguanidine, (b) a basic copper nitrate and (c) carboxymethyl cellulose sodium salt. In this case, contents are preferably 15 to 55% by weight of (a) nitroguanidine, 45 to 70% by weight of (b) a basic copper nitrate and 0.1 to 15% by weight of (c) carboxymethyl cellulose sodium salt.

[0067] Other preferable embodiment of the gas generating agent including the components (a), (b) and (c) can be one comprising (a) nitroguanidine, (b) a basic copper nitrate and (c) guar gum. In this case, contents are preferably 20 to 60% by weight, more preferably 30 to 50% by weight of (a) nitroguanidine, preferably 35 to 75% by weight, more preferably 40 to 65% by weight of (b) a basic copper nitrate, and preferably 0.1 to 10% by weight, more preferably 1 to 8% by weight of (c) guar gum.

[0068] Still other preferable embodiment of the gas generating agent including the components (a), (b) and (c) can be one comprising (a) nitroguanidine, (b) a basic copper nitrate, (c-1) guar gum and (c-2) a component (c) other than (c-1). In this case, contents are preferably 20 to 60% by weight, more preferably 30 to 50% by weight of (a) nitroguanidine, preferably 30 to 70% by weight, more preferably 40 to 60% by weight of (b) a basic copper nitrate, preferably 0.1 to 10%

by weight, more preferably 2 to 8% by weight of (c-1) guar gum, and preferably 0.1 to 10, more preferably 0.3 to 7% by weight of (c-2).

[0069] Still other preferable embodiment of the gas generating agent including the components (a), (b) and (c) can be one comprising (a) nitroguanidine, (b) a basic copper nitrate, (c-1) carboxymethyl cellulose sodium salt, (c-2) a component (c) other than (c-1). In this case, contents are preferably 15 to 50% by weight of (a) nitroguanidine, preferably 30 to 65% by weight of (b) a basic copper nitrate, preferably 0.1 to 15% by weight of (c-1) carboxymethyl cellulose sodium salt, and 1 to 40% by weight of (c-2).

[0070] Still other preferable embodiment of the gas generating agent including the components (a), (b) and (c) can be one comprising (a) dicyandiamide, (b) a basic copper nitrate and (c) carboxymethyl cellulose sodium salt. In this case, contents are preferably 15 to 25% by weight of (a) dicyandiamide, preferably 60 to 80% by weight of (b) a basic copper nitrate, and preferably 0.1 to 20% by weight of (c) carboxymethyl cellulose sodium salt.

[0071] Still other preferable embodiment of the gas generating agent including the components (a), (b) and (c) can be one comprising (a) dicyandiamide, (b) a basic copper nitrate, (c-1) carboxymethyl cellulose sodium salt, and (c-2) a component (c) other than (c-1). In this case, contents are preferably 15 to 25% by weight of (a) dicyandiamide, preferably 55 to 75% by weight of (b) a basic copper nitrate, preferably 0 to 10% by weight or 0.1 to 10% by weight of (c-1) carboxymethyl cellulose sodium salt, and 1 to 20% by weight of (c-2).

[0072] Still other preferable embodiment of the gas generating agent including the components (a), (b) and (c) can be one comprising (a) nitroguanidine, (b) strontium nitrate, (c-1) carboxymethyl cellulose sodium salt and (c-2) Japanese acid clay.

[0073] In the process of the invention, a combustion regulator (combustion improving agent) can be incorporated into the two or more starting components. The combustion improving agent is a component acting to improve combustion properties such as burning rate, duration of combustion, ignitability, etc. of the gas generating agent as a whole. As the combustion improving agent, at least one selected from the group consisting of silicon nitride, alkali metal or alkaline earth metal nitrites, nitrates, hydrochlorides or perchlorates (KNO_3 , NaNO_3 , KClO_4 , etc.), iron (III) oxide hydroxide [$\text{FeO}(\text{OH})$], copper oxide, iron oxide, zinc oxide, cobalt oxide and manganese oxide can be proposed. Among these, when iron (III) oxide hydroxide [$\text{FeO}(\text{OH})$] is used, combustion of the binder containing a large number of carbon atoms is improved excellently, thereby improving combustion of the gas generating agent as a whole.

[0074] An amount of the combustion improving agent blended is preferably 1 to 10 parts by weight, more preferably 1 to 5 parts by weight to the total (100 parts by weight) of the components (a) and (b) or the components (a), (b) and (c).

[0075] In the process of the invention, the gas generating agent can be molded in a desired shape, for example in the form of a single-perforated cylinder, a perforated (porous) cylinder, or a pellet.

[0076] The gas generating agent obtained in the process of the invention desirably satisfies one, two or three requirements selected from the following requirements (x), (y) and (z):

- (x) A shape of the molded article is in the form of a single-perforated cylinder or a perforated (porous) cylinder. By satisfying the requirement (x), the combustion area can be increased, so that combustion performance can be improved;
- (y) A reduced mass ratio of the molded article after being kept at 110°C for 400 hours is 1% or less, preferably 0.6% or less. By satisfying the requirement (y), thermal stability can be improved, so that the stable combustion performance can be maintained for a prolonged period of time; and
- (z) The mass reduction by heating of the molded article is 0.7% by weight or less, preferably 0.5% by weight or less, more preferably 0.3% by weight or less. By satisfying the requirement (z), the strength of the molded article can be maintained, so that the stable combustion performance can be maintained for a prolonged period of time.

[0077] When the moisture at the time of production of the gas generating agent is replaced by an equal volume of an organic solvent, for example, alcohols such as isopropanol, butanol, etc., esters such as ethyl acetate, etc., ethers such as isopropyl ethers, or ketones such as acetone, methyl ethyl ketone, etc., the mass reduction by heating of the molded article in the requirement (z) is 0.7% by weight or less, preferably 0.5% by weight or less, more preferably 0.3% by weight.

[0078] The gas generating agent obtained in the process of the invention can be applied to, for example, an air bag inflator for a driver side, an air bag inflator for a passenger side, an air bag inflator for a side collision, an inflator for an inflatable curtain, an inflator for a knee-bolster, an inflator for an inflatable seat belt, an inflator for a tubular system and an inflator for a pretensioner in various vehicles.

[0079] The gas generating agent obtained in the process of the invention can be used not only as the gas generating agent for inflators but also as an igniting agent called an enhancer (or booster) for transmitting the energy of a detonator or a squib to the gas generating agent.

Examples

[0080] Hereinafter, the present invention is described in more detail by reference to the examples, however, the present invention is not limited to these only.

Example 1 (Batch system)

[0081] As the starting components, 27.6% by weight of nitroguanidine, 33.0% by weight of a basic copper nitrate, 1.9% by weight of guar gum and 37.5% by weight of ion-exchanged water (electrical conductance, 1 $\mu\text{S}/\text{cm}$) were introduced into a kneader and mixed at the temperature of 70°C for 30 minutes.

[0082] After the starting components were mixed, the temperature inside the kneader was maintained at 80°C for 8 hours, and water vapor was removed by volatilization through a vent hole of the kneader. The content of moisture in the mixture was 15.5% by weight. Thereafter, the temperature of the mixture was reduced to 45°C under stirring in the kneader. Then, the mixture was removed from the kneader, transferred to an aging unit capable of regulating temperature, and aged for 8 hours at the temperature of at 40°C.

[0083] After aging, the mixture was fed to an extruder and molded at the molding pressure of 63 MPa to give a single-perforated strand. This strand was fed to a cutting machine and cut to give a single-perforated, cylindrical gas generating agent (having the outer diameter of 2.4 mm, the inner diameter of 0.7 mm, and the length of 4.0 mm).

[0084] Thereafter, the gas generating agent was placed in a drying oven, pre-dried at the temperature of 30°C and further dried at 80°C until the mass reduction by heating became 0.3% by weight or less, followed by sifting to give a final product.

[0085] The reduced mass ratio of the obtained gas generating agent after 400 hours was 0.4% by weight, which was determined in the thermal stability test described below. A lower reduced mass ratio indicates higher thermal stability, that is, decomposition hardly occurs even for a prolonged period of time (for example, for over 10 years).

(Thermal stability test)

[0086] 40 g of a gas generating agent was placed into an aluminum container, a total weight thereof was measured, and (total weight - weight of the aluminum container) was assumed to be the weight of the sample before the test. The aluminum container containing the sample was placed in an SUS thick container (having the internal volume of 118.8 ml), covered with a lid, and placed in a thermostat bath at 110°C. The container had been in a closed state by means of a rubber packing and a clamp. After a predetermined time passed, the SUS thick container was removed from the thermostat bath, and when the container was returned to room temperature, the container was opened, and the aluminum container was removed therefrom. The total weight of the sample inclusive of the aluminum container was measured, and (total weight - weight of the aluminum container) was regarded as the weight of the sample after the test. The thermal stability was evaluated by determining the reduced mass ratio by comparing the change in the weight before and after the test. The reduced mass ratio was obtained from $[(\text{weight of the gas generating agent before the test} - \text{weight of the gas generating agent after the test}) / \text{weight of the gas generating agent before the test}] \times 100$.

Claims

1. A process for producing a gas generating agent, which comprises

- a first step of feeding at least two starting components including a fuel and an oxidizing agent and stirring and mixing them in the presence of moisture, wherein the fuel is a nitrogen-containing compound, wherein the oxidizing agent is a basic metal nitrate, wherein the moisture is ion-exchanged water and/or distilled water, and wherein an amount of moisture in the mixture of the starting components is adjusted to 5 to 60% by weight,
- a second step of extrusion-molding the mixture and cutting it,
- a third step of drying it, wherein the mixture is dried so that an amount of moisture in the gas generating agent is reduced to 0.7% by weight or less, and

wherein the process further includes an aging step of keeping the mixture at 30 to 50°C for 8 hours or more between the first and second step.

2. The process for producing a gas generating agent according to claim 1, wherein, in the first step, each of the at least two starting components are fed with moisture and then mixed.

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3. The process for producing a gas generating agent according to claim 1, wherein, in the first step, the at least two starting components and moisture are simultaneously fed and then mixed.
- 5 4. The process for producing a gas generating agent according to claim 1, wherein, in the first step, the at least two starting components are mixed and simultaneously fed with moisture.
5. The process for producing a gas generating agent according to claim 1, wherein, in the first step, the at least two starting components are preliminarily mixed, then fed with moisture, and further mixed.
- 10 6. The process for producing a gas generating agent according to any one of claims 1 to 5, wherein the moisture is fed by spraying.
7. The process for producing a gas generating agent according to any one of claims 1 to 6, wherein the moisture has an electrical conductance of not higher than $2 \mu\text{S/cm}$, and is used in the form of an aqueous solution, water or
15 water vapor.
8. The process for producing a gas generating agent according to any one of claims 1 to 7, wherein the mixing conditions in the first step are the temperatures of 20 to 100°C and the time of 10 to 120 minutes.
- 20 9. The process for producing a gas generating agent according to any one of claims 1 to 7, wherein the mixing conditions in the first step are the temperatures of 20 to 100°C and the time of 1 to 10 minutes.
10. The process for producing a gas generating agent according to any one of claims 1 to 9, wherein, in the first step, the moisture is partially removed by volatilization while mixing.
- 25 11. The process for producing a gas generating agent according to any one of claims 1 to 10, wherein, in the first step, the moisture is partially removed by volatilization after mixing.
12. The process for producing a gas generating agent according to claim 11, wherein the moisture is removed by volatilization at a higher temperature by 0 to 80°C than the temperature at the time of mixing.
- 30 13. The process for producing a gas generating agent according to claim 10, 11 or 12, wherein, in the first step, the moisture is removed by volatilization so that an amount of moisture in the mixture of the starting components is reduced to 5 to 30% by weight.
- 35 14. The process for producing a gas generating agent according to any one of claims 1 to 13, wherein, in the first step, the moisture is partially removed by volatilization while mixing, and then cooling treatment is performed.
15. The process for producing a gas generating agent according to claim 14, wherein the temperature of the mixture after cooling treatment is 30 to 65°C .
- 40 16. The process for producing a gas generating agent according to claim 14 or 15, wherein the stirring rotation at the time of the cooling treatment is reversed and/or forwarded.
- 45 17. The process for producing a gas generating agent according to any one of claims 1 to 16, wherein an amount of moisture in the mixture of the starting compounds at the time of being transferred from the first step to the second step is 5 to 30% by weight.
18. The process for producing a gas generating agent according to any one of claims 1 to 16, wherein an amount of
50 moisture in the mixture of the starting compounds at the time of extrusion-molding in the second step is adjusted to 5 to 30% by weight.
19. The process for producing a gas generating agent according to any one of claims 1 to 16, wherein, at the time of extrusion molding in the second step, the mixture is pre-molded at the molding pressure of 70 MPa or less and then
55 molded at the molding pressure of 70 MPa or less.
20. The process for producing a gas generating agent according to claim 1, wherein, in the third step, the mixture is pre-dried at 20 to 40°C and then further dried at 80 to 120°C .

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21. The process for producing a gas generating agent according to any one of claims 1 to 20, which further includes classification treatment after the third step.
- 5 22. The process for producing a gas generating agent according to claim 21, wherein the nitrogen-containing compound is a guanidine derivative.
23. The process for producing a gas generating agent according to any one of claims 1 to 22, wherein the fuel is nitroguanidine, and the oxidizing agent is a basic copper nitrate.
- 10 24. The process for producing a gas generating agent according to any one of claims 1 to 23, wherein an additive is further included as the at least two starting components.
25. The process for producing a gas generating agent according to claim 24, wherein the additive is a binder and/or a slag-forming agent.
- 15 26. The process for producing a gas generating agent according to claim 25, wherein the viscosity of aqueous solution in 1 % by weight of the binder is 100 to 10,000 mPas.
- 20 27. The process for producing a gas generating agent according to claim 25 or 26, wherein the additive is guar gum or carboxymethyl cellulose sodium salt.
28. The process for producing a gas generating agent according to any one of claims 1 to 27, wherein, in the first step, an aqueous solution of the binder is fed as the moisture.
- 25 29. The process for producing a gas generating agent according to any one of claims 1 to 28, wherein there is obtained a molded article having one, two or three requirements selected from the following requirements (x), (y) and (z):
- (x) a shape of the molded article is in the form of a single-perforated cylinder or a perforated (porous) cylinder,
(y) a reduced mass ratio of the molded article after being kept at 110°C for 400 hours is 1% or less, and
30 (z) a mass reduction by heating of the molded article is 0.7% by weight or less.
- 30 30. The process for producing a gas-generating agent according to any one of claims 1 to 29, which includes the step of kneading and mixing the starting components in the presence of moisture by a screwed twin-shaft extruder.
- 35 31. The process for producing a gas generating agent according to claim 30, wherein the screwed twin-shaft extruder is a twin-screw extruder.
32. The process for producing a gas generating agent according to claim 30 or 31, which further includes the step of extrusion-molding and cutting the kneaded material and the step of drying it.
- 40 33. The process for producing a gas generating agent according to claim 30 or 31, which includes the step of kneading the mixture in a screwed twin-shaft extruder provided with a die in the extrusion orifice thereof in the kneading step, extrusion-molding it into an article of desired shape through the die, and immediately cutting it and the step of drying the article.
- 45 34. The process for producing a gas generating agent according to claim 30 or 31, which comprises the step of kneading the mixture in a screwed twin-shaft extruder provided with a die in the extrusion orifice thereof in the kneading step, extrusion-molding it through the die to give a molded article in the form of a strand and then cutting it and the step of drying it.
- 50 35. The process for producing a gas generating agent according to any one of claims 30 to 34, wherein an additive is further used as a starting component in the kneading step.
- 55 36. The process for producing a gas generating agent according to any one of claims 30 to 35, wherein, in the kneading step, the at least two starting components are preliminarily mixed and fed to a screwed twin-shaft extruder.
37. The process for producing a gas generating agent according to claim 36, wherein, when the starting components are three kinds of components i.e. fuel, an oxidizing agent and an additive, only the oxidizing agent and the additive

are preliminarily mixed, and the mixture and fuel are fed to a screwed twin-shaft extruder.

- 5
38. The process for producing a gas generating agent according to any one of claims 30 to 37, wherein the moisture is fed separately from the starting components to a screwed twin-shaft extruder, or the moisture is added to part or the whole of the starting components.
- 10
39. The process for producing a gas generating agent according to any one of claims 30 to 38, wherein the mixing conditions in the kneading step are the temperature of 20 to 100°C and the time of 1 to 10 minutes.
- 15
40. The process for producing a gas generating agent according to any one of claims 30 to 39, wherein, in the kneading step, the moisture is partially removed by volatilization while mixing.
- 20
41. The process for producing a gas generating agent according to any one of claims 30 to 40, wherein an amount of moisture in the mixture of the starting compounds at the time of being transferred from the kneading step to its subsequent step is 5 to 30% by weight.
- 25
42. The process for producing a gas generating agent according to any one of claims 30 to 41, wherein an amount of moisture in the mixture of the starting compounds at the time of molding or extrusion-molding in an extruder is adjusted to 5 to 30% by weight.
- 30
43. The process for producing a gas generating agent according to any one of claims 30 to 42, wherein the mixture is pre-molded at the molding pressure of 70 MPa or less at the time of molding and then molded at the molding pressure of 70 MPa or less.
- 35
44. The process for producing a gas generating agent according to any one of claims 30 to 43, which further includes classification treatment after the drying step.
- 40
45. The process for producing a gas generating agent according to claim 30, wherein the nitrogen-containing compound is a guanidine derivative.
- 45
46. The process for producing a gas generating agent according to any one of claims 30 to 45, wherein the fuel is nitroguanidine, and the oxidizing agent is a basic copper nitrate.
- 50
47. The process for producing a gas generating agent according to any one of claims 31 to 46, wherein an additive is further contained as the at least two starting compounds.
- 55
48. The process for producing a gas generating agent according to claim 30, wherein the additive is a binder and/or a slag-forming agent.
49. The process for producing a gas generating agent according to claim 48, wherein the viscosity of aqueous solution in 1 % by weight of the binder is 100 to 10,000 mPas.
- 50
50. The process for producing a gas generating agent according to claim 30 or 49, wherein the additive is guar gum or carboxymethyl cellulose sodium salt.
- 55
51. The process for producing a gas generating agent according to any one of claims 30 to 50, wherein an aqueous solution of the binder is fed as the moisture in the first step.
52. The process for producing a gas generating agent according to any one of claims 30 to 51, wherein there is obtained a molded article having one, two or three requirements selected from the following requirements (x), (y) and (z):
- (x) a shape of the molded article is in the form of a single-perforated cylinder or a perforated (porous) cylinder,
 - (y) a reduced mass ratio of the molded article after being kept at 110°C for 400 hours is 1% or less, and
 - (z) a mass reduction by heating of the molded article is 0.7% by weight or less.

Patentansprüche

1. Verfahren zum Herstellen eines gaserzeugenden Mittels, welches umfasst

- 5 - einen ersten Schritt des Zuführens von wenigstens zwei Ausgangskomponenten, die einen Treibstoff und ein Oxidationsmittel einschließen, und des Rührens und Mischens dieser in Gegenwart von Feuchtigkeit, wobei der Treibstoff eine stickstoffhaltige Verbindung ist, wobei das Oxidationsmittel ein basisches Metallnitrat ist, wobei die Feuchtigkeit ionenausgetauschtes Wasser und/oder destilliertes Wasser ist, und wobei eine Feuchtigkeitsmenge in der Mischung der Ausgangskomponenten auf 5 bis 60 Gew.-% eingestellt wird,
- 10 - einen zweiten Schritt des Extrudierens der Mischung und des Schneidens derselben,
- einen dritten Schritt des Trocknens derselben, wobei die Mischung so getrocknet wird, dass eine Feuchtigkeitsmenge in dem gaserzeugenden Mittel auf 0,7 Gew.-% oder weniger verringert wird, und

15 wobei das Verfahren außerdem einen Alterungsschritt, bei dem die Mischung 8 Stunden oder mehr bei 30 bis 50 °C gehalten wird, zwischen dem ersten und zweiten Schritt einschließt.

2. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 1, wobei in dem ersten Schritt jede von den wenigstens zwei Ausgangskomponenten mit Feuchtigkeit zugeführt und anschließend vermischt werden.

20 **3.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 1, wobei in dem ersten Schritt die wenigstens zwei Ausgangskomponenten und Feuchtigkeit gleichzeitig zugeführt und anschließend vermischt werden.

25 **4.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 1, wobei in dem ersten Schritt die wenigstens zwei Ausgangskomponenten vermischt und gleichzeitig mit Feuchtigkeit zugeführt werden.

30 **5.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 1, wobei in dem ersten Schritt die wenigstens zwei Ausgangskomponenten vorher vermischt werden, anschließend mit Feuchtigkeit zugeführt werden und weiter vermischt werden.

35 **6.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 5, wobei die Feuchtigkeit durch Sprühen zugeführt wird.

40 **7.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 6, wobei die Feuchtigkeit eine elektrische Leitfähigkeit von nicht höher als 2 μ S/cm aufweist und in Form von einer wässrigen Lösung, Wasser oder Wasserdampf verwendet wird.

45 **8.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 7, wobei die Mischbedingungen in dem ersten Schritt die Temperaturen von 20 bis 100 °C und die Zeit von 10 bis 120 Minuten sind.

50 **9.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 7, wobei die Mischbedingungen in dem ersten Schritt die Temperaturen von 20 bis 100 °C und die Zeit von 1 bis 10 Minuten sind.

55 **10.** Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 9, wobei in dem ersten Schritt die Feuchtigkeit durch Verflüchtigung während des Vermischens teilweise entfernt wird.

11. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 10, wobei in dem ersten Schritt die Feuchtigkeit durch Verflüchtigung nach dem Vermischen teilweise entfernt wird.

12. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 11, wobei die Feuchtigkeit durch Verflüchtigung bei einer Temperatur entfernt wird, die um 0 bis 80 °C höher ist als die Temperatur zum Zeitpunkt des Vermischens.

13. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 10, 11 oder 12, wobei in dem ersten Schritt die Feuchtigkeit durch Verflüchtigung entfernt wird, so dass eine Feuchtigkeitsmenge in der Mischung der Ausgangskomponenten auf 5 bis 30 Gew.-% verringert wird.

14. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 13, wobei in dem ersten Schritt die Feuchtigkeit durch Verflüchtigung während des Vermischens teilweise entfernt wird und anschließend

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eine Kühlungsbehandlung durchgeführt wird.

- 5
15. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 14, wobei die Temperatur der Mischung nach der Kühlungsbehandlung 30 bis 65 °C beträgt.
16. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 14 oder 15, wobei die Rührrotation zum Zeitpunkt der Kühlungsbehandlung rückwärts und/oder vorwärts gerichtet ist.
- 10
17. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 16, wobei eine Feuchtigkeitsmenge in der Mischung der Ausgangsverbindungen zum Zeitpunkt der Überführung von dem ersten Schritt zu dem zweiten Schritt 5 bis 30 Gew.-% beträgt.
18. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 16, wobei eine Feuchtigkeitsmenge in der Mischung der Ausgangsverbindungen zum Zeitpunkt des Extrudierens in dem zweiten Schritt auf 5 bis 30 Gew.-% eingestellt wird.
- 15
19. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 16, wobei zum Zeitpunkt des Extrudierens in dem zweiten Schritt die Mischung bei dem Pressdruck von 70 MPa oder weniger vorgeformt und anschließend bei dem Pressdruck von 70 MPa oder weniger geformt wird.
- 20
20. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 1, wobei in dem dritten Schritt die Mischung bei 20 bis 40 °C vorgetrocknet und anschließend bei 80 bis 120 °C weiter getrocknet wird.
21. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 20, welches außerdem eine Klassierungsbehandlung nach dem dritten Schritt einschließt.
- 25
22. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 21, wobei die stickstoffhaltige Verbindung ein Guanidinderivat ist.
- 30
23. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 22, wobei der Treibstoff Nitroguanidin ist und das Oxidationsmittel ein basisches Kupfernitrat ist.
24. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 23, wobei außerdem ein Additiv als die wenigstens zwei Ausgangskomponenten eingeschlossen ist.
- 35
25. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 24, wobei das Additiv ein Bindemittel und/oder ein schlackenbildendes Mittel ist.
26. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 25, wobei die Viskosität der wässrigen Lösung in 1 Gew.-% des Bindemittels 100 bis 10000 mPas beträgt.
- 40
27. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 25 oder 26, wobei das Additiv Guargummi oder Carboxymethylcellulose-Natriumsalz ist.
- 45
28. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 27, wobei in dem ersten Schritt eine wässrige Lösung des Bindemittels als die Feuchtigkeit zugeführt wird.
29. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 28, wobei ein Formkörper erhalten wird, der eine, zwei oder drei Anforderungen, ausgewählt aus den folgenden Anforderungen (x), (y) und (z), aufweist:
- 50
- (x) eine Gestalt des Formkörpers ist in Form eines einfach perforierten Zylinders oder eines perforierten (porösen) Zylinders,
(y) ein reduziertes Massenverhältnis des Formkörpers, nachdem er 400 Stunden bei 110 °C gehalten wurde, beträgt 1 % oder weniger, und
(z) eine Massenreduktion durch Erwärmen des Formkörpers beträgt 0,7 Gew.-% oder weniger.
- 55
30. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 1 bis 29, welches den Schritt

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des Knetens und Mischens der Ausgangskomponenten in Gegenwart von Feuchtigkeit durch einen Zweiwellen-Schneckenextruder einschließt.

- 5
31. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 30, wobei der Zweiwellen-Schneckenextruder ein Doppelschneckenextruder ist.
- 10
32. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 30 oder 31, welches außerdem den Schritt des Extrudierens und Schneidens des gekneteten Materials und dem Schritt des Trocknens desselben einschließt.
- 15
33. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 30 oder 31, welches den Schritt des Knetens der Mischung in einem Zweiwellen-Schneckenextruder, der mit einer Düse in seiner Extrusionsöffnung versehen ist, in dem Knetschritt, des Extrudierens derselben zu einem Artikel mit einer gewünschten Gestalt durch die Düse und des sofortigen Schneidens desselben und den Schritt des Trocknens des Artikels einschließt.
- 20
34. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 30 oder 31, welches den Schritt des Knetens der Mischung in einem Zweiwellen-Schneckenextruder, der mit einer Düse in seiner Extrusionsöffnung versehen ist, in dem Knetschritt, des Extrudierens derselben durch die Düse, um einen Formkörper in Form eines Strangs zu erhalten, und anschließend des Schneidens desselben und den Schritt des Trocknens desselben umfasst.
- 25
35. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 34, wobei außerdem ein Additiv als eine Ausgangskomponente in dem Knetschritt verwendet wird.
- 30
36. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 35, wobei in dem Knetschritt die wenigstens zwei Ausgangskomponenten vorher vermischt und einem Zweiwellen-Schneckenextruder zugeführt werden.
- 35
37. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 36, wobei, wenn die Ausgangskomponenten drei Arten von Komponenten sind, d. h., Treibstoff, ein Oxidationsmittel und ein Additiv, nur das Oxidationsmittel und das Additiv vorher vermischt werden und die Mischung und der Treibstoff einem Zweiwellen-Schneckenextruder zugeführt werden.
- 40
38. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 37, wobei die Feuchtigkeit getrennt von den Ausgangskomponenten einem Zweiwellen-Schneckenextruder zugeführt wird oder die Feuchtigkeit zu einem Teil oder dem Ganzen der Ausgangskomponenten zugegeben wird.
- 45
39. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 38, wobei die Mischbedingungen in dem Knetschritt die Temperatur von 20 bis 100 °C und die Zeit von 1 bis 10 Minuten sind.
- 50
40. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 39, wobei in dem Knetschritt die Feuchtigkeit durch Verflüchtigung während des Vermischens teilweise entfernt wird.
- 55
41. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 40, wobei eine Feuchtigkeitsmenge in der Mischung der Ausgangsverbindungen zum Zeitpunkt der Überführung von dem Knetschritt zu seinem nachfolgenden Schritt 5 bis 30 Gew.-% beträgt.
42. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 41, wobei eine Feuchtigkeitsmenge in der Mischung der Ausgangsverbindungen zum Zeitpunkt der Formgebung oder des Extrudierens in einem Extruder auf 5 bis 30 Gew.-% eingestellt wird.
43. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 42, wobei die Mischung bei dem Pressdruck von 70 MPa oder weniger zum Zeitpunkt der Formgebung vorgeformt und anschließend bei dem Pressdruck von 70 MPa oder weniger geformt wird.
44. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 43, welches außerdem eine Klassierungsbehandlung nach dem Trocknungsschritt einschließt.
45. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 30, wobei die stickstoffhaltige Verbindung

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ein Guanidinderivat ist.

5 46. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 45, wobei der Treibstoff Nitroguanidin ist und das Oxidationsmittel ein basisches Kupfernitrat ist.

47. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 31 bis 46, wobei außerdem ein Additiv als die wenigstens zwei Ausgangsverbindungen enthalten ist.

10 48. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 30, wobei das Additiv ein Bindemittel und/oder ein schlackenbildendes Mittel ist.

49. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 48, wobei die Viskosität einer wässrigen Lösung in 1 Gew.-% des Bindemittels 100 bis 10000 mPas beträgt.

15 50. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß Anspruch 30 oder 49, wobei das Additiv Guargummi oder Carboxymethylcellulose-Natriumsalz ist.

20 51. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 50, wobei eine wässrige Lösung des Bindemittels als die Feuchtigkeit in dem ersten Schritt zugeführt wird.

52. Verfahren zum Herstellen eines gaserzeugenden Mittels gemäß einem der Ansprüche 30 bis 51, wobei ein Formkörper erhalten wird, der eine, zwei oder drei Anforderungen, ausgewählt aus den folgenden Anforderungen (x), (y) und (z), aufweist:

25 (x) eine Gestalt des Formkörpers ist in Form eines einfach perforierten Zylinders oder eines perforierten (porösen) Zylinders,

(y) ein reduziertes Massenverhältnis des Formkörpers, nachdem er 400 Stunden bei 110 °C gehalten wurde, beträgt 1 % oder weniger, und

(z) eine Massenreduktion durch Erwärmen des Formkörpers beträgt 0,7 Gew.-% oder weniger.

Revendications

35 1. Procédé de production d'un agent générateur de gaz, qui comprend

40 - une première étape consistant à apporter au moins deux composants de départ parmi lesquels un combustible et un comburant et à les agiter et les mélanger en présence d'humidité, où le combustible est un composé contenant de l'azote, le comburant est un nitrate de métal basique, l'humidité est de l'eau désionisée et/ou de l'eau distillée et où une quantité d'humidité dans le mélange des composants de départ est réglée pour être de 5 à 60 % en poids,

- une deuxième étape consistant à mouler par extrusion le mélange et à le découper,

- une troisième étape consistant à le sécher, le mélange étant séché de sorte qu'une quantité d'humidité dans l'agent générateur de gaz est réduite à 0,7 % en poids ou moins, et

45 où le procédé inclut en outre une étape de vieillissement consistant à maintenir le mélange de 30 à 50 °C pendant 8 heures ou plus entre la première et la deuxième étape.

50 2. Procédé de production d'un agent générateur de gaz selon la revendication 1, où, à la première étape, chacun des aux moins deux composants de départ sont alimentés en humidité puis mélangés.

3. Procédé de production d'un agent générateur de gaz selon la revendication 1, où, à la première étape, les aux moins deux composants de départ et l'humidité sont apportés simultanément puis mélangés.

55 4. Procédé de production d'un agent générateur de gaz selon la revendication 1, où, à la première étape, les aux moins deux composants de départ sont mélangés et alimentés simultanément en humidité.

5. Procédé de production d'un agent générateur de gaz selon la revendication 1, où, à la première étape, les au moins deux composants de départ sont préalablement mélangés, puis alimentés en humidité, puis de nouveau mélangés.

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6. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 5, où l'humidité est apportée par pulvérisation.
- 5 7. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 6, où l'humidité a une conductance électrique non supérieure à $2 \mu S/cm$, et est utilisée sous la forme d'une solution aqueuse, d'eau ou de vapeur d'eau.
- 10 8. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 7, où les conditions de mélange à la première étape sont les températures de 20 à 100 °C et le temps de 10 à 120 minutes.
- 15 9. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 7, où les conditions de mélange à la première étape sont les températures de 20 à 100 °C et le temps de 1 à 10 minutes.
- 20 10. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 9, où, à la première étape, l'humidité est partiellement éliminée par volatilisation pendant le mélange.
- 25 11. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 10, où, à la première étape, l'humidité est partiellement éliminée par volatilisation après le mélange.
- 30 12. Procédé de production d'un agent générateur de gaz selon la revendication 11, où l'humidité est éliminée par volatilisation à une température supérieure de 0 à 80 °C à la température au moment du mélange.
- 35 13. Procédé de production d'un agent générateur de gaz selon la revendication 10, 11 ou 12, où, à la première étape, l'humidité est éliminée par volatilisation de sorte qu'une quantité d'humidité dans le mélange des composants de départ est réduite à 5 à 30 % en poids.
- 40 14. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 13, où, à la première étape, l'humidité est partiellement éliminée par volatilisation pendant le mélange, puis un traitement de refroidissement est effectué.
- 45 15. Procédé de production d'un agent générateur de gaz selon la revendication 14, où la température du mélange après le traitement de refroidissement est de 30 à 65 °C.
- 50 16. Procédé de production d'un agent générateur de gaz selon la revendication 14 ou 15, où la rotation d'agitation au moment du traitement de refroidissement est inversée et/ou avancée.
- 55 17. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 16, où une quantité d'humidité dans le mélange des composés de départ au moment du transfert de la première étape à la deuxième étape va de 5 à 30 % en poids.
18. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 16, où une quantité d'humidité dans le mélange des composés de départ au moment du moulage par extrusion à la deuxième étape est réglé pour être de 5 à 30 % en poids.
19. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 16, où, au moment du moulage par extrusion à la deuxième étape, le mélange est pré-moulé à la pression de moulage de 70 MPa ou moins puis moulé à la pression de moulage de 70 MPa ou moins.
20. Procédé de production d'un agent générateur de gaz selon la revendication 1, où, à la troisième étape, le mélange est pré-séché à une température de 20 à 40 °C puis encore séché à une température de 80 à 120 °C.
21. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 20, qui inclut en outre un traitement de classification après la troisième étape.
22. Procédé de production d'un agent générateur de gaz selon la revendication 21, où le composé contenant de l'azote est un dérivé de guanidine.
23. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 22, où le

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combustible est de la nitroguanidine, et le comburant est un nitrate de cuivre basique.

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24. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 23, où un additif est également inclus en tant que les au moins deux composants de départ.
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25. Procédé de production d'un agent générateur de gaz selon la revendication 24, où l'additif est un liant et/ou un agent formant des scories.
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26. Procédé de production d'un agent générateur de gaz selon la revendication 25, où la viscosité d'une solution aqueuse dans 1 % en poids du liant va de 100 à 10 000 mPas.
- 20
27. Procédé de production d'un agent générateur de gaz selon la revendication 25 ou 26, où l'additif est de la gomme de guar ou un sel sodique de carboxyméthylcellulose.
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28. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 27, où, à la première étape, une solution aqueuse du liant est apportée en tant que l'humidité.
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29. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 28, où l'on obtient un article moulé ayant une, deux ou trois exigences choisies parmi les exigences (x), (y) et (z) suivantes :
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- (x) une forme de l'article moulé présente la forme d'un cylindre à une seule perforation ou d'un cylindre perforé (poreux),
- (y) un rapport de réduction massique de l'article moulé après maintien à 110 °C pendant 400 heures est de 1 % ou moins, et
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- (z) une réduction massique par chauffage de l'article moulé est de 0,7 % en masse ou moins.
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30. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 1 à 29, qui inclut l'étape consistant à malaxer et mélanger les composants de départ en présence d'humidité par une extrudeuse à deux arbres filetés.
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31. Procédé de production d'un agent générateur de gaz selon la revendication 30, où l'extrudeuse à deux arbres filetés est une extrudeuse bivis.
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32. Procédé de production d'un agent générateur de gaz selon la revendication 30 ou 31, qui inclut en outre l'étape consistant à mouler par extrusion et à découper le matériau malaxé et l'étape consistant à le sécher.
33. Procédé de production d'un agent générateur de gaz selon la revendication 30 ou 31, qui inclut l'étape consistant à malaxer le mélange dans une extrudeuse à deux arbres filetés équipée d'une filière dans son orifice d'extrusion lors de l'étape de malaxage, à le mouler par extrusion en un article de forme souhaitée à travers la filière et à le découper immédiatement et l'étape consistant à sécher l'article.
34. Procédé de production d'un agent générateur de gaz selon la revendication 30 ou 31, qui comprend l'étape consistant à malaxer le mélange dans une extrudeuse à deux arbres filetés équipée d'une filière dans son orifice d'extrusion lors de l'étape de malaxage, à le mouler par extrusion à travers la filière pour obtenir un article en forme de fil puis à le découper et l'étape consistant à le sécher.
35. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 34, dans lequel un additif est également utilisé en tant que composant de départ lors de l'étape de malaxage.
36. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 35, où, lors de l'étape de malaxage, les au moins deux composants de départ sont mélangés au préalable et introduits dans une extrudeuse à deux arbres filetés.
37. Procédé de production d'un agent générateur de gaz selon la revendication 36, où, lorsque les composants sont trois types de composants, c'est-à-dire du combustible, un comburant et un additif, seuls le comburant et l'additif sont préalablement mélangés, et le mélange et le combustible sont introduits dans une extrudeuse à deux arbres filetés.

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38. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 37, où l'humidité est introduite séparément des composants de départ dans une extrudeuse à deux arbres filetés, ou l'humidité est ajoutée à une partie ou à la totalité des composants de départ.
- 5 39. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 38, où les conditions de mélange lors de l'étape de malaxage sont les températures de 20 à 100 °C et le temps de 1 à 10 minutes.
- 10 40. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 39, où, lors de l'étape de malaxage, l'humidité est partiellement éliminée par volatilisation pendant le mélange.
- 15 41. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 40, où une quantité d'humidité dans le mélange des composés de départ au moment du transfert de l'étape de malaxage à l'étape suivante va de 5 à 30 % en poids.
- 20 42. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 41, où une quantité d'humidité dans le mélange des composés de départ au moment du moulage ou du moulage par extrusion dans une extrudeuse est réglé pour être de 5 à 30 % en poids.
- 25 43. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 42, où le mélange est pré-moulé à la pression de moulage de 70 MPa ou moins au moment du moulage et ensuite moulé à la pression de moulage de 70 MPa ou moins.
- 30 44. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 43, qui inclut en outre un traitement de classification après l'étape de séchage.
- 35 45. Procédé de production d'un agent générateur de gaz selon la revendication 30, où le composé contenant de l'azote est un dérivé de guanidine.
- 40 46. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 45, où le combustible est de la nitroguanidine, et le comburant est un nitrate de cuivre basique.
- 45 47. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 31 à 46, où un additif est également inclus en tant que les au moins deux composés de départ.
- 50 48. Procédé de production d'un agent générateur de gaz selon la revendication 30, où l'additif est un liant et/ou un agent formant des scories.
- 55 49. Procédé de production d'un agent générateur de gaz selon la revendication 48, où la viscosité d'une solution aqueuse dans 1 % en poids du liant va de 100 à 10 000 mPas.
- 50 50. Procédé de production d'un agent générateur de gaz selon la revendication 30 ou 49, où l'additif est de la gomme de guar ou un sel sodique de carboxyméthylcellulose.
- 55 51. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 50, où une solution aqueuse du liant est apportée en tant que l'humidité à la première étape.
52. Procédé de production d'un agent générateur de gaz selon l'une quelconque des revendications 30 à 51, où l'on obtient un article moulé ayant une, deux ou trois exigences choisies parmi les exigences (x), (y) et (z) suivantes :
- (x) une forme de l'article moulé présente la forme d'un cylindre à une seule perforation ou d'un cylindre perforé (poreux),
(y) un rapport de réduction massique de l'article moulé après maintien à 110 °C pendant 400 heures est de 1 % ou moins, et
(z) une réduction massique par chauffage de l'article moulé est de 0,7 % en masse ou moins.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 5487851 A [0004]
- US 5565150 A [0004]
- US 5670098 A [0004]
- JP 10087390 A [0005]
- JP 9110574 A [0006]
- JP 11310490 A [0007]
- EP 458443 A [0008]
- EP 458439 A [0009]
- WO 9622954 A [0010]
- US 5735118 A [0011]
- EP 820971 A [0012]
- EP 1061057 A [0013]
- WO 9806486 A [0014]
- US 5608183 A [0015]
- EP 0694511 A [0016]